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<b>(54) Title:</b> DIMENSION STABLE BINDING AGENT SYSTEMS		
<b>(57) Abstract</b>  Chemically bound ceramic system, the binder phase of which essentially consisting of a cement based system, which material comprises one or more expansion compensating additives adapted to give the material dimension stable long time properties.		

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## DIMENSION STABLE BINDING AGENT SYSTEMS

### TECHNICAL FIELD

The present invention relates to a chemically bound ceramic material, the binder phase  
5 of which essentially consisting of a cement based system. The primary use for the material is as a dental filling material.

### BACKGROUND OF THE INVENTION

The present invention relates to binding agent systems of the cement system type,  
10 especially the system  $\text{CaO-Al}_2\text{O}_3\text{-(SiO}_2\text{)-H}_2\text{O}$ . This system is used in the building industry for exceptionally hard and tough environments, i.e. acid environments with a high mechanical stress (R J Mangabhai, Calcium Aluminate Cements, Conference volume, E & F N Spon, London 1990). By applying rupture mechanical methods and advanced powder technique on the system, the generally good properties profile of the  
15 base system can be considerably improved. Studies in connection with the invention and previous work (SE patent 463 493 and 502 987) have given results which point at a great potential for the system for strong and acid resistant materials as dental filling materials. No dental filling material existing today fulfils all the requirements as to bio-compatibility, aesthetics and function, which may be posed by patients and dental care  
20 personnel. The situation for different dental filling materials may be concluded according to the following. Amalgam exhibits a generally good strength, but exhibits flaws when it comes to bio-compatibility and aesthetics. Plastic composites exhibit a good workability, but exhibit flaws when it comes to erosion and corrosion and in handling for the personnel (allergy problems arisen). Plastic composites shrink at the  
25 hardening, which leads to a risk of formation of gaps and, over a time period, caries attack. Glass ionomers exhibit a good binding to dentine, and enamel, but exhibit flaws when it comes to corrosion and strength. Silicate cement exhibits a good compression strength and aesthetics, but suffers from corrosion and strength problems. Different types of inserts exhibit good mechanical properties, but are work demanding and require  
30 gluing.

In the following there is given a description of the requirements which generally should be posed for a new practical dental filling material; A good manageability with easy applicability in cavities, a workability which permits a good ability of modelling, a  
35 hardening/solidification which is fast enough for the filling work and functioning directly after the dentist appointment. Furthermore, there is required a high level of strength and corrosion resistance, which exceeds the one for existing filling materials, a

good bio-compatibility, good aesthetics and a secure handling for the personnel, without additives in the materials which may cause allergies or which are toxic. Also, there is required good long time properties in the form of dimension stability. Especially it is a problem if the material expands over time, which may result in fatal tooth bursts.

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It has been previously shown, in Swedish patent 502 987, that a complete hydration (which was believed to lower the risk of dimension changes) in a cement system, may take place if a complete soaking and a thereafter following compaction of the cement system is made by aid of a specially designed stopper. The method does however not prevent dimension changes which take place later on and which are related to phase transitions in hydrates or reactions with the surrounding environment (as for example exhalation air with an increased content of carbon dioxide), or other reactions. These reactions and related dimension changes are more noticeable in cases where a high compaction degree is used in the production of the material. A higher compaction degree is however normally desired, since it generally leads to a better strength.

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In Yan et al, Characteristics of shrinkage compensation expansive cement containing pre-hydrated high alumina cement-based expansive additive, Cement and Concrete Research, Vol. 24, p 267-276 (1990), the use of the tendency of calcium aluminates to expand, is described. This article and related work on expansive cements describe the possibilities to get standard cement to expand or shrink less, with the use e.g. calcium aluminates, but does not discuss the problems of long time expansion of highly compacted systems or controlling of the expansion of calcium aluminates to very low levels, which is necessary for the use of these binding agent systems in applications according to the present invention.

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Other related work and patents, which however do not discuss the basic ideas of the present invention, are for example SE-B-381 808, EP-A-0 024 056 and EP-A-0 115 058, DE 5 624 489 and US-A-4 689 080.

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#### DESCRIPTION OF THE INVENTION

It is an object of the present invention to provide a material of the type described in the introduction, which material exhibits dimension stable long time properties. The material should also, for dental applications, fulfil the requirements which according to the above are posed for such materials.

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This is accomplished according to the invention by the material comprising one or more expansion compensating additives adapted to give the material dimension stable long time properties.

- 5 Chemical properties are, besides good mechanical properties, important for dental applications. In one important aspect of the invention, calcium aluminates, i.e. double oxides of CaO (calcium oxide) and Al<sub>2</sub>O<sub>3</sub> (aluminium oxide) – here and below denoted the CA system, which react with water under formation of calcium aluminate hydrates, are used as the main binder phase. This hydration reaction constitutes the setting and  
10 hardening process itself. To the calcium aluminate cements there are conventionally added some type of aggregates (filler particles), essentially for economic reasons. According to the invention, the choice of the CA cement system, combined with some other cement system or a phase which interacts with the aluminate cements, or combined with an addition of porous aggregates or soft particles, enables a dimension  
15 change which is below about 0.20 % linearly, often below 0.10%. In special cases, the dimension change may be close to zero expansion.

- According to a first embodiment of the invention, the CA system may be used as the sole main binder phase, or with an addition of another cement binder phase in contents  
20 decreasing 30 vol-%. Advantageously, there is used additions of ordinary Portland cement (OPC cement) or fine grain silica. While calcium aluminate cements have a tendency to expand seriously at more dense compaction, the combination of CA cement and other phases of the above mentioned type, with the tendency to shrink, may give decreased dimension changes. The CA cements should, in dental applications, be the  
25 main phase in the binder phase, since the CA phase contributes to a good strength and acid resistance.

- It has become clear that the theories relating to causes for dimension changes, which theories were put forward in connection with SE patent 502 987, i.e. incomplete  
30 hydration, do not seem to fully explain the reasons behind the problems in dimension stability. The background of the present invention is more an apprehension that the dimension changes are connected with hydrate phase transitions. This statement, which should not be seen as limiting for the invention, means that calcium aluminate, when it is beginning to be dissolved at the addition of water, forms a gel which thereafter  
35 crystallises and forms hydrate phases. By subsequent hydration reactions and hydrate transitions, different pure Ca-aluminate hydrates as 10-phase, 8-phase, other less defined hydrate phases or transition phases, and finally 6-phase (katoit) may exist, and

in the case of silicon containing additives, Ca-Si-aluminate hydrates. By 10-phase, 8-phase and 6-phase it is hereby meant Ca-aluminate phases with 10, 8 and 6 crystal waters respectively, per formula unit. The phase transition of the hydrates may lead to dimension changes, especially expansion, which has been shown by long time  
5 evaluation of cement materials. In connection with the present invention, it has surprisingly been found that at an addition of a silicon containing secondary phase, preferably ordinary so called Portland cement (OPC cement with Ca-silicates as main phases) and/or fine crystalline silica (which constitutes said first, preferred embodiment of the invention), unwanted phase transitions may be essentially avoided or the phase  
10 transition sequence may be altered, and as a direct consequence thereof, dimension changes may be minimised, especially long time expansion. It is not yet fully clarified how the complicated hydration reactions take place in detail. By addition of Si containing materials, the hydration reactions are modified, which gives dimension stable materials.

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It has surprisingly been found that the just mentioned positive effects in connection with the addition of a secondary phase exhibit an optimum at relatively low amounts added. The smallest expansion has thereby been achieved when said secondary phase is OPC cement and/or fine crystalline silica and/or some other Si containing phase, preferably  
20 in a total content of 1-20 vol-% and even more preferred 1-10 vol-% in the material. Most preferably, said secondary phase is OPC cement in a content of 1-5 vol-% and/or fine crystalline silica in a content of 1-5 vol-%. There is also referred to the examples in the present description.

25 It has also surprisingly been found that conventional hardness contributing filler particles, e.g. in the form of hard  $\text{Al}_2\text{O}_3$  particles, may be entirely avoided in the material, or that their use may be minimised, since it is hydrate transitions that are the primary cause for dimension changes over time, especially long time changes. The expansion compensating additives according to the invention thereby act on the cement  
30 phase, without any effect of hardness contributing filler particles possibly being present. The fact that it is possible to avoid or minimise the use of hardness contributing filler particles further depend on remaining non-reacted cement – which previously was considered serious from expansion point of view – only giving a minor contribution to the expansion. In connection with the invention it has become clear that non-reacted  
35 cement on the contrary acts positively, as an in situ filler material, which contributes to the desired hardness of the material.

According to another embodiment of the invention, the dimension stability of the considered binding agent systems may be thoroughly controlled and controlled to the desired levels, most often to low levels or no dimension change at all, by addition of aggregates (filler particles) with a given geometry/shape, porosity and/or softness.

- 5 Below, the situation for the cement system  $\text{CaO-Al}_2\text{O}_3\text{-(SiO}_2\text{)-H}_2\text{O}$ , which advantageously may be used as a base material for dental filling materials, is described in more detail, but the invention is generally relating to ceramic binding agent systems where the dimension stability is critical.
- 10 By choosing aggregates (filler particles) in binding agent systems according to the present invention with a specific geometry and porosity, the binding conditions between the binder phase and aggregates, as well as the dimension stability, may be positively affected. Porous aggregates and other expansion or shrink compensating additives accordingly contribute to the possibilities to control the dimension changes to a desired
- 15 level by acting as "expansion vessel".

- The function of porous aggregates according to the present invention is accordingly to be able to increase the contact surface with the cement phase and to distribute it on smaller extension areas, while retaining a high given content of filler particles. The
- 20 expansion which originates from the cement phase is primarily taken care of by the porous filler particle, by giving the cement a possibility to expand inside the same. Porous aggregates may advantageously be inert ceramic materials such as aluminium dioxide, zirconium oxide, titanium oxide or zinc oxide or some other oxide or combination of oxides. The porosity may be an open or a closed porosity or a
- 25 combination thereof. In the normal case, the porous particle or the aggregate has an open porosity of 20-60 %, preferably 30-50 %- The size of the aggregates is optimally chosen in adaptation to the rupture toughness of the materials, but most often exhibit a diameter below 20  $\mu\text{m}$ , preferably 5-15  $\mu\text{m}$ . In the considered materials, small porous aggregates or particles contribute to finer surfaces (lower  $R_a$ -values) than do solid
- 30 particles of the corresponding size. The pore openings in the aggregates are adapted to the penetration capacity of the binders. Beneficially, the pore openings are less than 5  $\mu\text{m}$ , preferably 0.1-5  $\mu\text{m}$  and even more preferred 1-3  $\mu\text{m}$ .

- Porous aggregates or particles of the above mentioned oxides are preferably produced
- 35 by sintering fine grain powder, however not at too high temperatures in order for the aggregates or particles to be maintained porous. Aluminium oxide is for example advantageously sintered at about 1500-1600°C. The sintering process is controlled to a

desired diameter, porosity and size of pores. Alternatively, the porous aggregates or particles may be produced by fine grain oxide powder being mixed with a compound, e.g. starch, which is brought to evaporate in order to form pores. The material is freeze granulated by being sprayed and frozen.

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In a special case, in order to be able to absorb inner tensions created by dimension changes in the binder phase, aggregates with a very high closed porosity may be used, which aggregates burst at a high inner tension to give an internal expansion room. The content of these highly porous particles is limited to 5 vol-% of the binder phase at a maximum. Highly porous microspheres of glass may thereby be used. The highly porous materials are added to the cement mixer in the end of the mixing operation in order to avoid grinding of them. In another special case, a very soft particle is chosen as an additive, which may absorb tensions by having a coefficient of elasticity which decreases the one for the binder phase. In this case there may be used different soft polymers, e.g. plastic balls, or hydrates. When plastic balls are used, which are very small, these may possibly exhibit holes in the middle, for additional deformability.

According to one aspect of the invention it has also become clear that the dimension stability of the material may be increased by the included components being brought to exhibit a high level of fine grains. This is also true for strength aspects. The theory is that too large particles have a tendency to be clamped in the structure, which results in different properties in different directions. According to one aspect of the invention there is therefore used a fine grain, finely distributed mixture of binder raw materials which gives a fine, homogenous micro structure. Small areas of extension for the included phases will decrease the inner mechanical tension between phases, and admit an improved possibility for compensation of the internal expansion which may take place in connection with the alteration of phases, such as a continued reaction with the surroundings or phase transitions. The size which may be permitted depends on what level of strength that is desired, typically however, the grain size should have a distribution over 0.5-10  $\mu\text{m}$ . The calcium aluminates are brought through grinding to essentially exhibit a grain size of about 2-8  $\mu\text{m}$ , preferably 3-4  $\mu\text{m}$  or about 3  $\mu\text{m}$ , and OPC cement, when such is used, is by grinding brought to essentially exhibit a grain size of about 4-8  $\mu\text{m}$ , preferably 5-7  $\mu\text{m}$  or about 6  $\mu\text{m}$ . Fine grain silica, when such is used, should exhibit an even smaller grain size, preferably in the magnitude of below 100 nm, and even more preferred about 10-50 nm, e.g. about 15 nm, which is a type of silica that for example may be bought as a trade merchandise, having been separated in an electrostatic filter in connection with the production of silicon.



The invention is further described in the following examples of embodiments.

#### EXAMPLE

- 5 A series of tests were performed in order to study the effect of different expansion compensating additives on expansion, especially on long time expansion.

##### *Description of raw materials:*

- 10 Calcium aluminates of the phases  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$  included in e.g. Ca-aluminate cement (Alcoa and Lafarge alternatively), standard cement (Cementa), fine grain silica (Aldrich) and glass spheres (Sil-cell, Stauss GmbH).  $\text{Al}_2\text{O}_3$  (Sumitomo, AKP 30),  $\text{ZrO}_2$  (3-mol%  $\text{Y}_2\text{O}_3$ ) from Toyo Soda.

Porous particles, self made by fine grain Al-oxide (Sumitomo, AKP 30) (aggregate diameter ca 15 micrometer).

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##### *The examples a)-h) below describe*

- a) long time expansion of calcium aluminate in a completely hydrated aluminate without additives, but with hardness contributing filler particles (reference)  
b) effect of fine grain level in the cement raw material  
20 c) effect of secondary phase, OPC cement  
d) effect of secondary phase, fine grain Si-oxide  
e) effect of porous aggregate on b)  
f) effect of porous aggregate on c)  
g) effect of the combination of OPC and fine grain Si-oxide  
25 h) effect of the combination of different additives  
i) effect of Si containing secondary phases on a pure cement system without hardness contributing filler particles  
j) effect of hardness contributing filler particles on i)

- 30 Calcium aluminates,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ , with a molar ratio of about 1:1 is mixed with filler particles and secondary additives (all given contents in relation to the content of calcium aluminate) according to the below. When "aluminium oxide" is mentioned without the type of particles being specified, conventional hardness contributing filler particles are intended.

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- a) addition of 40 vol-% aluminium oxide, grinding time 24 h. The cement was previously ground during 20 h.

- b) addition of 40 vol-% aluminium oxide, grinding time 24 h. The cement was previously ground during 80 h.
  - c) addition of 40 vol-% aluminium oxide, grinding time 24 h. The cement was previously ground according to b) above. To the calcium aluminate there is added 5 15 vol-% OPC (ordinary Portland cement/standard cement).
  - d) addition of 40 vol-% aluminium oxide, grinding time 24 h. To previously ground calcium aluminate according to b) above, there is added a secondary phase in the form of 10 vol-% fine grain silica.
  - e) addition of 20 vol-% aluminium oxide, grinding time 24 h. The cement was 10 previously ground according to b) above. 20 vol-% porous aluminium oxide aggregates (self made) is added only after a grinding time of 20 h.
  - f) addition of 20 vol-% aluminium oxide + 20 vol-% aluminium oxide in the form of porous particles (aggregates), grinding time 24 h, the aggregates being added only after 20 h. The cement was previously ground according to b) above, however with 15 an addition of a secondary phase in the form of 15 vol-% OPC.
  - g) addition of 40 vol-% aluminium oxide, grinding time 24 h. The cement was previously ground according to b) above. To the calcium aluminate there is added 5 vol-% OPC and 5 vol-% fine grain silica.
  - h) addition of 20 vol-% aluminium oxide + 20 vol-% aluminium oxide in the form of 20 porous particles (aggregates), grinding time 24 h, the aggregates being added only after 20 h. To the calcium aluminate there is in this case added an secondary phase in the form of 5 vol-% OPC and 5 vol-% fine grain silica and 0.5 vol-% glass spheres.
  - i) addition of secondary phases in the form of 5 vol-% OPC and 5 vol-% fine grain 25 silica, grinding time 24 h. The cement was previously ground during 80 h.
  - j) addition of secondary phases in the form of 5 vol-% OPC and 5 vol-% fine grain silica and hardness contributing filler particles of 10 vol-%  $\text{ZrO}_2$ , grinding time 24 h. The cement was previously ground during 80 h.
- 30 The mixtures are ground in a ball mill with inert milling balls of silicon nitride with a filling degree of 35 %. As liquid there is used isopropanol. The materials a)-h) were soaked in water after the solvent having been driven off, and were dewatered and filled with a stopper into a hole with a diameter of 4 mm in a container which permitted measuring of the dimensions in an optical microscope. The material were kept moist at 35 37 °C between the sample measurements, which were performed continuously during up to 180 days.

The result is shown in the table below.

Sample	Expansion in % after				
	1d	20d	80d	120d	180d
5					
a	0	0.12	0.68	0.82	0.83
b	0	0.22	0.41	0.48	0.48
c	0	0.11	0.23	0.26	0.26
d	0	0.12	0.13	0.13	0.13
10 e	0	0.15	0.18	0.21	0.21
-----					
f-j	all values below 0.10 %				

The marginal of error at the measurements is  $\pm 0.02$  %.

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From the results it can be concluded that the expansion stagnates after about 100 days. For the materials which are very dimension stable (expansion below 0.10 %), no evident point in time when stagnation occurs can be found. Furthermore it is clear that

- An increased grinding time (b) in itself, in relation to the reference (a), almost halves the long time expansion.
- When, in addition to this, there is added a secondary phase in the form of OPC cement at a content of 15 vol-% (c), there is almost achieved an additional halving of the long time expansion in relation to (b).
- With a secondary phase in the form of fine grain silica at a content of 10 vol-% (d), the long time expansion is even more decreased.
- Also with porous aggregates of aluminium oxide at a content of 20 vol-% (e), there is achieved an improved (decreased) long time expansion in relation to (b).
- Extremely low expansions were achieved when porous particles and a secondary phase of OPC cement was used in combination.
- Extremely low expansions were achieved when secondary phase of both OPC cement and fine grain silica was used in combination.
- Extremely low expansions were achieved when porous particles, a secondary phase of both OPC cement and fine grain silica and glass spheres was used in combination.
- Extremely low expansions were achieved in the pure cement system, without any hardness contributing filler particles, when only a low content of a Si-containing additive was used.

- An extremely low expansion was achieved in the Ca-aluminate system including low contents (10 vol-%) of hardness contributing filler particles, when only Si-containing additives were used for expansion compensation.
- 5 The materials which exhibit an extremely low expansion ( $< 0.10\%$ ) have, in addition to the expansion properties, a generally good property profile which corresponds to the corresponding cement system without additive. These materials exhibit a compression strength of about 200 MPa, a hardness of H (Vickers 100 g) = 150, and an extremely good resistance to acid.

## CLAIMS

1. Chemically bound ceramic system, the binder phase of which essentially consisting of a cement based system, c h a r a c t e r i s e d i n that the material comprises one or more expansion compensating additives adapted to give the material dimension stable long time properties.
2. Material according to claim 1, c h a r a c t e r i s e d i n that the material is intended to be used for dental purposes, preferably as or in dental filling materials.
3. Material according to claim 1 or 2, c h a r a c t e r i s e d i n that a dimension change, after an initial solidification of the material, is 0.20 % linear change at the most, and preferably less than 0.10 % linear change.
4. Material according to any of the above claims, c h a r a c t e r i s e d i n that the material is essentially free from hardness contributing filler particles.
5. Material according to any of the above claims, c h a r a c t e r i s e d i n that said binder phase at least mainly consists of calcium aluminate cement.
6. Material according to any of the above claims, c h a r a c t e r i s e d i n that said additive is one or more additives in the group that consists of porous particles or porous aggregates, soft particles and secondary phase, which secondary phase reacts with the binder phase.
7. Material according to claim 6, c h a r a c t e r i s e d i n that said additive at least mainly consists of a secondary phase, said secondary phase preferably consisting of OPC cement and/or fine crystalline silica and/or some other Si-containing phase, preferably at a total content of 1-20 vol-% and even more preferred 1-10 vol-%, in the material.
8. Material according to claim 7, c h a r a c t e r i s e d i n that said secondary phase consists of OPC cement at a content of 1-5 vol-% and/or fine crystalline silica at a content of 1-5 vol-%.
9. Material according to claim 6, c h a r a c t e r i s e d i n that said additive at least mainly consists of porous particles or porous aggregates, preferably exhibiting a

diameter of 2-30  $\mu\text{m}$ , even more preferred 5-15  $\mu\text{m}$ , an open porosity of 20-60 %, preferably 30-50 %, and the pore openings in the particles/aggregates being less than 5  $\mu\text{m}$ , preferably less than 0,1-5  $\mu\text{m}$  and even more preferred 1-3  $\mu\text{m}$ .

- 5 10. Material according to claim 9, c h a r a c t e r i s e d i n that said porous particles or porous aggregates at least mainly consist of oxides of Al, Zr, Ti, Si or Zn.
11. Material according to claim 6, c h a r a c t e r i s e d i n that said additive at least mainly consists of porous particles, which porous particles at least mainly consist of  
10 microspheres with a high closed porosity, which microspheres preferably are made of glass and exhibit a porosity which exceeds 50%, preferably exceeds 80%.
12. Material according to claim 11, c h a r a c t e r i s e d i n that said microspheres are included at contents below 2 vol-% of the material, preferably 0.1-2 vol-%, and even  
15 more preferred 0.5-1.5 vol-%.
13. Material according to claim 6, c h a r a c t e r i s e d i n that said additive at least mainly consists of soft particles, which soft particles exhibit a coefficient of elasticity which decreases the coefficient of elasticity of the binder phase.